

COMBUSTION CHARACTERISTICS AND EMISSIONS
FROM BURNING ORGANIC SOILS

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Introduction

Organic soils cover many millions of hectares in the United States,⁽¹⁾ including 2.8 million hectares in the Southern United States and about 1.0 million in south Florida⁽²⁾. Organic soils form when plants such as pond weeds, grasses, shrubs, and trees die and are covered by water for extended periods. With oxygen excluded, decomposition is very slow. As residues accumulate, layers of organic material are formed producing a record of plant succession. These accumulations can approach 10 meters in thickness where water levels don't fluctuate. Where the organic debris is exposed during dry periods--such as in south Florida--depths are generally less than 5 meters. As the water level recedes, the top soil layer is oxidized and its color darkens.

If these soils are sufficiently dry, they will support combustion when ignited by faster spreading surface fires. The danger of this happening is especially great on drained areas. The presence of layers and/or pockets of charcoal in south Florida soil profiles, however, document a history of periodic fire extending back several thousand years.

Organic soils are generally consumed by smoldering fires that can last for months, burning down to the water table before going out. These slow burning fires (horizontal rates of spread in the range of several meters per day) produce visible smoke when burning near the surface but can become remarkably smoke free as they burn through deeper layers. Combustion is evident from a general haze over the area combined with a disagreeable and pungent odor from partially oxidized organic material. These soils can, however, burn more rapidly and produce copious amounts of smoke around deep fissures in the soil or where the soil is overturned.

Benner⁽³⁾ examined emissions from gram-size samples burned in an environmental chamber. However, he induced and sustained combustion with an external heat source (hot wire) rather than observing natural combustion. From qualitative analyses, McFarlane⁽⁴⁾ and Skiotis, et al.⁽⁵⁾ report some organic constituents of "peat" smoke from studies designed to identify the flavor characteristics of scotch whiskey. To our knowledge, there have been no quantitative analyses emissions from smoldering combustion of organic soil.

The Southern Forest Fire Laboratory began a study in 1976 to learn more about this process. Field studies of soil burning would be very costly because the soil combustion rate is uncertain and it is difficult to collect representative emission samples. We, therefore, decided to measure emissions from small blocks of burning soil in the laboratory.

Core samples of organic soil were collected in south-central Florida and transferred to our combustion laboratory at Macon, Georgia. The samples were burned in a manner which simulated the slow smoldering that is common in the field. This paper reports soil combustion characteristics and emissions of several criteria pollutants. Further work on the chemical characterization of the particulate matter emissions is underway and will be reported separately.

Before describing the experimental details and results, some organic soil characteristics will be briefly summarized.

Organic Soil Characteristics

In the current system of soil identification, organic soils are classified as Histosols.⁽⁶⁾ A Histosol must have at least 20 to 30% organic matter (many have more than 90%). Common terminology includes bog, marsh, moor muskeg, peat, and muck. The terms peat and muck are often used synonymously in the literature but are actually quite different types of organic soil. Peats are organic materials that have undergone little decomposition; they are usually coarse textured, and low in mineral content (0 to 35%). Muck soils are high in mineral content (35 to 75%), and are thoroughly decomposed. The well-known sphagnum peats are formed mainly from sphagnum mosses along with ferns, sedges, and shrubs. Large areas of sphagnum peats are found in Alaska, Canada, and northern parts of Maine and Minnesota. These peat deposits represent a major potential source of energy and hydrocarbons. The energy equivalent in U. S. peat reserves has been estimated by the Institute of Gas Technology to be about 1443 quads or 240 billion bbl of oil.⁽⁷⁾ Another type of organic soil is formed chiefly from reeds and grasses in shallow lakes, swamps, and meadows. The sawgrass peats of the Florida Everglades are of this type. The Everglades contain 75% of the organic soil acreage in Florida and comprises the largest contiguous body of organic soils in the United States. Here, organic soils are important not only to the natural ecology, but also to multimillion dollar sugar cane and truck crop industries on drained areas. Because of these values and the proximity of organic soils to populated areas, there is much concern whenever these soils burn. Moreover, the heightened awareness of air quality has focused attention on the contribution of these fires to local and regional air pollution.

Chemical Characteristics of Organic Soils

Physical and chemical changes during organic soil formation influence ignition potential, the burning process, and the products of combustion. According to Bear,⁽⁸⁾ organic compounds make up between 20 and 95% of the total dry weight of peat and muck soils. Virtually all is of plant origin. Included are cellulose, hemicellulose, lignin and lignin derivatives, and a variety of fats, waxes, and resins. The proportions of the various substances depend on (a) plants from which the soil was derived, (b) stage of decomposition of the several layers, and (c) nature of the associated water. Cellulose and hemicellulose are susceptible to microbial decomposition and their content in organic soils is considerably lower than that of the original plants. The sawgrass plant of the Florida Everglades contains about five to seven times as much cellulosic material as does sawgrass peat. As shown in Table I, there is about three times as much ash in the peat as in the sawgrass plant, about four times the crude protein, and a definite increase in lignin. Lignin content often increases with depth in the peat deposit.

Table I Organic composition of the sawgrass plant and sawgrass peat. (a)

Material analyzed	Ash	Crude protein	Hemi- cellulose	Cellulose	Lignin
-----Percent of dry weight-----					
<u>Sawgrass peat</u>					
Upper layer	9.9	22.7	7.1	0.3	44.6
Lower layer	11.6	20.8	6.0	0.2	48.0
<u>Sawgrass plant</u>	3.7	5.5	21.1	29.5	30.0

(a)

Adapted from Davis. (2)

The nitrogen content of organic soils varies from approximately 0.7 to 3.5%. Soils developed from reeds, sedges, grasses, and forest vegetation usually range between 1.5 and 3.0% nitrogen. (8)

Sulfur is present in peat and muck soils--largely in the organic form derived from the original plant material. The quantity found ranges from 0.05 to 0.25% in the sphagnum peats to 0.2 to 1.5% in the soils derived from reeds, grasses, and forest vegetation. (8)

Physical Characteristics of Organic Soils

Among the various physical properties of organic soils, the high water-absorbing capacity is one of the most relevant characteristics pertaining to this study. Waksman⁽⁹⁾ reported that sawgrass peats absorb water equivalent to 400 to 800% of their dry weight, whereas sphagnum peats are able to absorb as much as 800 to 2000%. Interestingly, peat, once dried, is not readily rewet by water. Poor reabsorption of water by dried peat is an important consideration in the management and suppression of organic soil fires. When a peat bog is partly or fully drained, the peat is subject to aerobic decomposition. This process causes the peat to settle.

The differences in structure and composition of organic soils cause them to vary a great deal in weight, density, and specific gravity. Davis⁽²⁾ reports dry specific gravity of peats to range between 0.11 and 1.03. Waksman⁽⁹⁾ found the specific gravity of sawgrass peats to range between 0.50 and 0.63. High porosity, which is found in nearly all fibrous peats, strongly influences the fire behavior.

In Florida, organic soil fires generally occur during the height of the dry season when surface fire incidence is at its peak. Advances made on suppression of the surface fires during the day are often reversed during the night when smoldering soil fires reignite the surface fuels. Nighttime work on organic soil fires is especially hazardous. Practically no light is cast

by the fire, and vegetation continually falls over as supporting roots are consumed. Furthermore, the fires can burn out deep pits, or spread horizontally, leaving a thin unburned top crust that will cave in under a person's weight.

Perhaps the biggest obstacle to organic soil fire suppression is that these soils are difficult to rewet, especially from above. For example, in 1975, approximately 105,000 gallons of water were needed to extinguish a 4-acre muck fire near Bartow, Florida. Often chunks of burning soil will float on a flooded burn area for days. Flooding is the usual method of fire suppression, but the lack of a sufficient water source and the logistics of transporting these required volumes often combine to preclude its use. One somewhat successful method is to bury the burning organic material under a layer of packed mineral soil.

The Florida Division of Forestry⁽¹⁰⁾ describes methods for combating fires in organic soils of various textures, depths, and moisture regimes. The report contains several effective methods when organic soils are shallow, but as the soils get deeper less effective control methods have to be used. When the organic soil is shallow or the water table is near the surface, heavy equipment can be used to build firelines down to mineral soil or to saturated organic soil. However, when these soils are wet, heavy equipment is easily mired.

Materials and Methods

Sample Collection and Preparation

Soil samples were obtained near Gordonville, in Polk County, Florida. Soils at the sample site are classified in the Hontoon series of Histosols. This series consists of nearly level, very poorly drained organic soils that occur frequently in fresh water swamps and marshes. Samples of the soil's upper layer were collected by forcing opened 2-gallon (21.6 cm h x 21.6 cm dia) paint containers into the ground. Samples were sealed in the containers and stored at room temperature. Just prior to burning, 24 to 30 1/4-inch holes were drilled in a uniform pattern into the sides of the can to allow for air circulation and to permit small (< 100 mg) samples to be removed for moisture analysis. Care was taken to remove a small sample so as not to affect the burning pattern.

The subsamples were immediately analyzed for moisture, percent organics, and ash content with a Perkin-Elmer TGS-2 thermogravimetric analyzer.^(a) From samples not used in the combustion experiments, larger subsamples were taken and submitted for chemical analysis. Carbon and hydrogen contents were measured by C,H,N analyzer; N by C,H,N analyzer and Kjeldahl; and S by LECO sulfur analyzer.

(a)

Mention of trade names throughout this Paper does not constitute endorsement by the U. S. Department of Agriculture.

Sample Properties

A total of six samples (three wet, three dry) were burned. Some properties of these samples are outlined in Table II.

Table II. Soil properties for combustion experiments.

Experiment no.	Sample wet wt g	Moisture content ^{a/} wt %	Ash content ^{a/} wt %	Density	
				wet g cm ⁻³	dry g cm ⁻³
wet soils					
M 5	3089	53	5.3	.52	.34
M10	3848	76	7.8	.60	.34
M 6	4663	97 ^{b/}	6.2	.63	.32
dry soils					
M 7	1768	7.2	19.7	.26	.24
M 8	2844	6.0	10.7	.42	.40
M 9	2199	6.7	16.5	.33	.31

^{a/} Average of three samples taken from 4, 10, and 17 cm levels; calculated on a dry weight basis.

^{b/} Lower portion of soil contained 135% moisture.

The wet samples were used as taken from the ground. The dry samples were oven-dried for several hours to lower the moisture content below 10% of dry weight. Although all the samples were taken from the same general area, there are clearly moisture gradients, soil layering, and other discontinuities that make it difficult to obtain true sample replication. However, the results permit general observations about emissions and soil burning characteristics.

Soil pooled from core samples not used in the burning experiments had the following chemical constituents: carbon $50.2 \pm 1.4\%$; hydrogen $5.2 \pm 0.3\%$; nitrogen $1.5 \pm 0.2\%$, and sulfur $0.30 \pm 0.08\%$. These are within the ranges of values previously reported for soils derived from reeds, grasses, and forest vegetation. ^(2,8)

Combustion Experiments

The natural surface of the soil was exposed by cutting out the bottom of the container (Figure 1). The general arrangement for the combustion experiments is shown in Figure 2. This arrangement was selected after several unsuccessful attempts to obtain self-sustained combustion in small (10 to 25 cm) cubes of organic soil. The small cubes would go out after a few minutes. The technique



A-BEFORE BURNING



B-AFTER BURNING

FIGURE 1. PHOTOGRAPHS OF CONTAINER USED IN
SOIL COMBUSTION EXPERIMENTS.

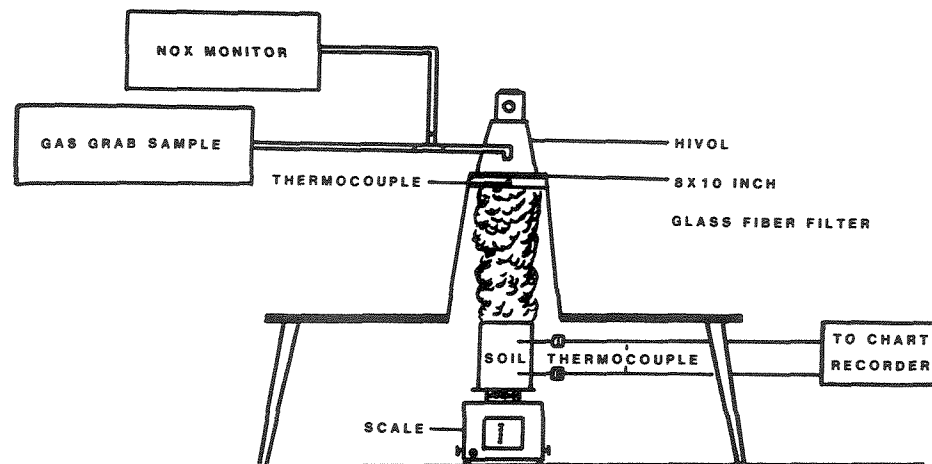


FIGURE 2. ILLUSTRATION OF SOIL
COMBUSTION APPARATUS

described herein proved successful in obtaining a sustained slow combustion that simulated the natural burning process. We had difficulty in igniting some of the samples. For dry samples, with some exposed plant root structure, a brief exposure to a propane torch was sufficient. For the wet samples, ignition was achieved by cutting a small (8-cm long, 2-cm deep) wedge on the surface and then applying the torch for 2 to 5 minutes. This may seem to be a somewhat unrealistic ignition procedure, but it should be remembered that natural fires in these soils often start from a surface fuel element burning in a soil fissure. Furthermore, the ignition technique did not significantly affect the subsurface moisture as shown by several moisture samples taken after combustion had been underway for several hours. Time-lapse photography was used to monitor weight-loss at night. Subsurface combustion temperatures were monitored by a chromel/alumel thermocouple located in the center of the soil mass. For samples M9 and M10, two thermocouples at 7 and 17 cm depths were used.

At periodic intervals during the burning, emissions were monitored by moving a metal hood equipped with a high-volume sampler over the soil container. The sampler was operated at $20 \text{ ft}^3 \text{ min}^{-1}$. A second thermocouple monitored gas temperatures at the surface of the sampler. A glass-fiber filter was used to collect particulate matter emissions. Collection temperatures at the filter surface were normally between 30°C and 40°C . These short sampling periods combined with the relatively low collection temperatures allowed for efficient collection and retention of particulate matter on the filter. Weights of aluminum foil strips fastened to the interior of the metal hood were taken before and after burning; they indicated negligible amounts of particulate clinging to the hood. Gaseous emissions were sampled by pumping a prefiltered sample through teflon tubing into a gas sampling bag. The bags were aluminized 5-layer polymeric bags whose storage characteristics are described by Thrun.⁽¹¹⁾ Pump flow rates were adjusted to provide a full bag over the time period sampled. Immediately after sample collection, the gas bag was taken to a chemiluminescence (CL), NO_x analyzer (NO and NO_2). NO_x loss was less than 5 percent, if analyzed within 15 minutes. For experiments M9 and M10, the CL monitor was set up to analyze NO_x on a real-time basis. A flame ionization/gas chromatographic method was initially intended for CO and total hydrocarbon (THC) analyses. However, mechanical problems with the chromatograph prevented its extensive use. A nondispersive infrared monitor was also used for CO analysis. Moisture, ash content, and emission factors were calculated on a dry weight basis.

Particulate Matter Analysis

The filter samples were weighed, wrapped in aluminum foil, and stored at 15°C . A portion of the filter was extracted with methylene chloride and the extract was separated into strong acid, weak acid, basic, and neutral fractions. Details of this procedure and further separation of the neutral fraction into subfractions will be reported separately.

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Benzo(a)pyrene (BaP) Analysis

An aliquot of the neutral fraction was chromatographed on a model 601 Perkin-Elmer liquid chromatograph equipped with a model 204 fluorescence detector. Reverse phase chromatography on an octadecyl column (Perkin-Elmer HC-ODS-SIL-X, 25 x 0.26 cm) was successful at a flow rate of 1 ml per minute with 75% methanol in water at 30°C column temperature. The detector's excitation wavelength was set at 381 nm and the emission wavelength at 403 nm.

Results and Discussion

Combustion Characteristics

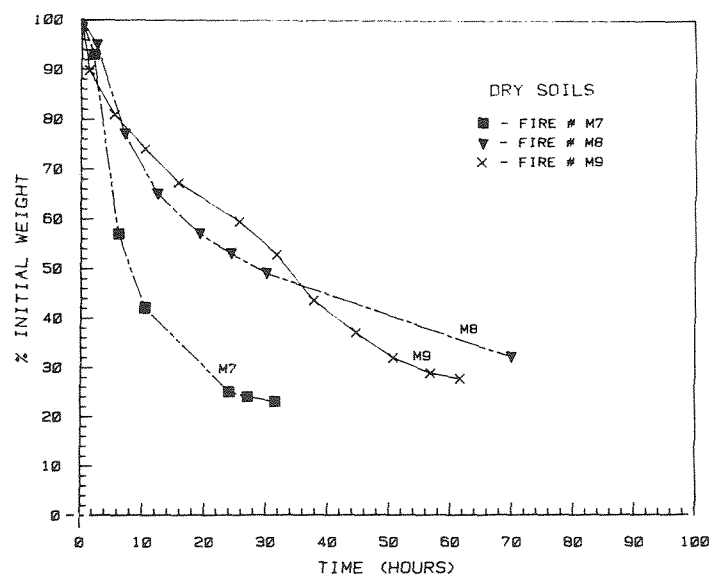
Samples burned slowly, but continued to burn for several days (Figure 3). Weight-loss rates ranged from a low of 0.2 g min^{-1} to a high of 6.3 g min^{-1} . The combustion zone would initially move downward from the point of ignition and begin to spread horizontally to the sides of the container. Often, the fuel near the surface did not burn completely until many hours of subsurface burning had taken place. Initially, the wet samples burned more slowly than the dry samples. However, after some moisture was evaporated, a crust of dry, unburned surface fuels would collapse, bringing air and dry fuel into the reaction zone. Combustion and smoke production were greatly influenced by these events.

All samples burned to a grey ash with only minor amounts of black char and unburned soil remaining. There was never any evidence of gas phase flaming combustion. In fact, the ash mantle obscured the glowing combustion zone. After the surface fuels were consumed, the thermocouple readings and pungent odor were often the only physical evidence of combustion. The insulating properties of the ash mantle are believed to contribute to self-propagation of smoldering combustion in these soils.

Ohlemiller, et al.⁽¹²⁾ have studied the smoldering process in flexible polyurethane foams and suggest that the self-insulating character of the smolder process makes it viable in a wide range of fuel conditions if the ignition stimulus is sufficiently long. Their model also implies that in all porous fuels heat conduction and radiation dictate smolder propagation. On the other hand, they suggest that the intensity of the smolder, as measured by its heat generation rate, is almost entirely controlled by oxygen supply. The smoldering process is flexible enough to adapt to a wide range of oxygen-supply levels, including extraordinarily low levels.

Moist organic soil can sustain smoldering combustion when the heat generated exceeds that lost from the combustion zone. Initially, a high temperature ignition source (i.e., surface fires, propane torch, etc.) may be required for a long period to overcome heat losses from the top of the fuel, once an insulating layer of partially consumed fuel and ash builds up, however, sustained smoldering will occur. This same fundamental process has been suggested in modeling work on coal-bed burning and tobacco combustion,⁽¹²⁾ and can be expected to apply to the combustion of municipal waste dumps and other smoldering processes.

A



B

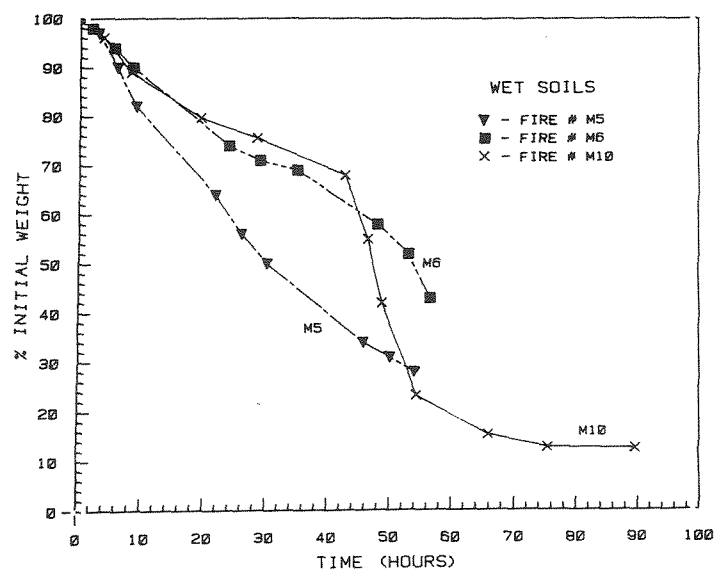


FIGURE 3. Burning behavior for organic soils:
(A) Dry soils; (B) Wet soils.

The most obvious conclusion one can make from these observations is that moist organic soils above the water table will support combustion if the ignition source is of sufficient duration and intensity. Certainly an overall fuel moisture content of 100% cannot be presumed to preclude smoldering, especially if there are small, dry humps or patches within a given area that can act as fire starters. These experiments clearly demonstrate that organic soils fires once started can dry and burn through fuel layers that contain up to 135% moisture (Table II).

Combustion Temperatures

Peak temperatures as registered in the center of the soil mass are shown in Table III.

Table III. Temperature maximum for organic soil fires.

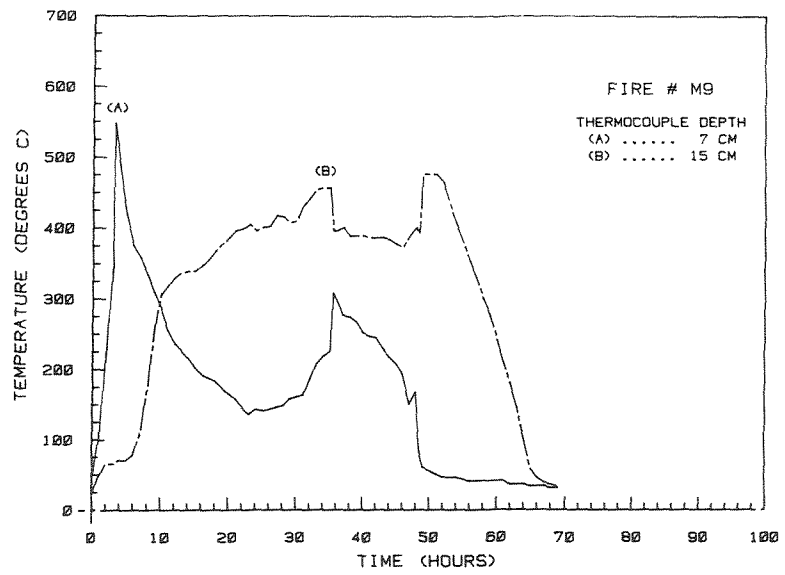
Experiment no.	Average moisture wt %	Temperature maximum °C depth	
		7 cm	15 cm
Wet soils			
M 5	53	458	
M10	76	484	512
M 6	97 ^{a/}	416	
Dry soils			
M 7	6	625	
M 8	7	502	
M 9	7	548	477
^{a/} Lower portion of soil contained 135% moisture.			

Temperatures were slightly higher in the dry soil samples. The 625°C reached in sample M7 was higher than the other samples. This sample had the lowest bulk density and burned more rapidly. With more oxygen available, a more intense fire resulted with subsequent higher temperatures. Typical time-temperature profiles are shown in Figure 4 and illustrate the extraordinarily long residence times encountered in these experiments. Note the number of hours above 100°C and 300°C. The peak temperatures reported here are typical of temperatures reported for other smoldering combustion processes, e.g., polyurethane foams, cigarettes, and cellulosic fuels, and are much below the peak flame temperatures (900°C to 1400°C) reported in the open burning of forest and piled woody fuels.^(13,14)

The relatively low temperatures and long residence times found in smoldering combustion of carbonaceous fuels have been cited as major causes of the evolution of high concentrations of toxic and irritating emissions such as aldehydes, phenols, and carbon monoxide.^(15,16)

A

80-15.5



B

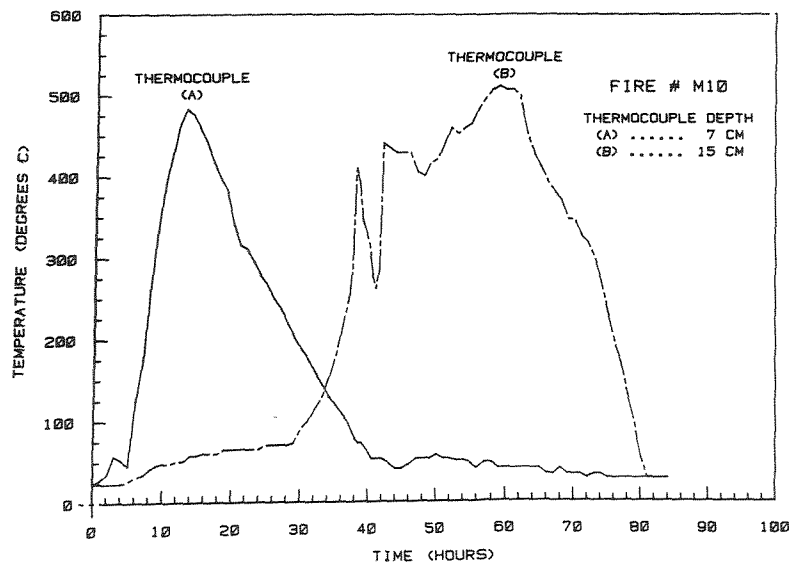


Figure 4 Time temperature profiles of organic soil
combustion: (A) Dry soil: (B) Wet soil.....

Emissions

Emission factors for the soil experiments are shown in Table IV. The data are shown for each sampling interval in order to illustrate the wide variability in burning rates and emissions. The total suspended particulate matter (TSP) emission factors ranged from below 1 g kg^{-1} to above 60 g kg^{-1} . In general, the dry soils produced high emission factors for the first 24 hours of burning ($30 \pm 20 \text{ g kg}^{-1}$)^(b) and dramatically lower factors ($1 \pm 1 \text{ g kg}^{-1}$) for the latter stages when combustion rates dropped and the ash layer prevented air from entering the combustion zone. The reverse was true for the wet soils; $4.1 \pm 3.8 \text{ g kg}^{-1}$ for the first 24 hours and $25 \pm 20 \text{ g kg}^{-1}$ for the later periods. In the wet soils, the high emission rates occurred after fuels near the surface dried and collapsed into the burning zone in the center of the can. The dramatic rise in emission rates can be seen in experiments 6 and 10. This may have also occurred in experiment 5, however, no emission measurements were made beyond 27 hours. The particulate matter emitted in these fires appeared as bright yellow oil droplets on the surface of the glass fiber collection filter. No soot particles were evident. Although particle sizes were not measured, prior work with the pyrolysis of peat by Skiotis, et al.⁽⁵⁾ has shown the aerodynamic diameter to be less than 1 micron. This is consistent with combustion theory and findings for other slow combustion processes such as cigarette smoke and smoldering wood.

(b)

Mean \pm standard deviation.

The solubility of the particulate matter in methylene chloride was extraordinarily high ($94 \pm 5.6\%$). Of this, $63 \pm 11\%$ was found to be in the so-called neutral fraction which contains many long-chain saturated hydrocarbons, polynuclear aromatic hydrocarbons, and other complex high-molecular weight organic compounds. A more detailed chemical characterization of the particulate matter is underway and will be reported separately. In 13 TSP samples analyzed for benzo(a)pyrene (BaP), concentrations of BaP averaged $319 \mu\text{g kg}^{-1}$ and ranged from 13 to $1178 \mu\text{g kg}^{-1}$. These values are within the range reported for burning pine needles⁽¹⁷⁾ and hardwood leaves.⁽¹⁸⁾

Carbon monoxide (CO) emission factors were very high in all experiments, with highest values toward the end of the fires when much of the fuel had reached a charred state. The dry fuels averaged $274 \pm 130 \text{ g kg}^{-1}$ and the wet fuels gave similar results ($263 \pm 139 \text{ g kg}^{-1}$). These unusually high CO emission factors suggest that large organic soil fires could contribute significantly to ambient CO concentrations and should be considered in regional emission inventories. Concentrations approaching 100 ppm can be expected in the vicinity of large area soil fires.

Total hydrocarbons (THC), as measured by a flame ionization detector, averaged $24 \pm 18 \text{ g kg}^{-1}$ for the dry soils and $21 \pm 11 \text{ g kg}^{-1}$ for the wet soils. Nitrogen oxides (NO_x) emission factors were low in all fires due to the very low combustion temperatures which prevented the formation of thermally derived nitric oxide (NO) via the Zeldovich mechanism. The low NO_x values in these

Table IV. Emission factors for organic soils^{a/}

Elapsed Time Hours	Weight Remaining %	Weight loss rate g min ⁻¹	TSP	Emission Factor			BaP µg kg ⁻¹
				CO	THC	NO _x ^{b/}	
-----g kg ⁻¹ -----							
Emission factors for dry organic soils							
1.2	91	3.3	51.9	172	32	0.3	234
1.7	87	6.6	25.2	114	11	0.2	127
4.0	64	2.1	51.9	295	36	0.8	249
6.0	53	1.3	63.2	414	67	1.5	293
1.5	98	1.8	48.0			0.3	409
2.5	93	2.2	30.0			0.3	265
4.0	88	2.6	33.0			0.3	397
6.0	81	0.8	41.0			2.3	1178
7.0	77	1.4	10.0			1.7	
25.5	54	0.3	0.4			5.1	
26.5	53	0.3	0.4	240		4.7	
28.5	53	0.2	0.4			5.9	
30.0	52	0.2	0.2			6.3	
1.0	90	1.9	25.0	167	20	0.6	
3.6	84	1.6	5.5	130	12	0.9	
5.8	80	0.5	4.1	275	33	2.1	
24.5	60	0.4	6.5	308	13	0.6	
29.0	55	0.3	3.0	363	12	0.5	
52.7	30	0.2	1.1	543	6	1.6	
Emission factors for wet organic soils							
2.3	96	1.4	10.6			0.5	168
4.4	91	1.2	7.0	197		1.6	13
7.4	84	1.2	2.6	180		0.6	
27.5	52	0.7	0.9	217		2.4	
3.1	96	0.8	3.9			1.8	
5.3	94	0.8	6.1			2.2	46
7.0	91	0.9	1.9			2.2	
26.0	72	0.4	0.6			2.6	
49.0	56	0.8	5.1			0.5	
53.5	51	1.6	13.3			0.7	89
54.8	47	2.3	55.3			1.0	675
2.2	99	0.8	10.0	252	17	0.7	
7.2	93	1.2	2.0	201	15	0.9	
19.3	79	0.3	0.1	236	17	2.1	
25.9	77	0.3	0.1	232	13	1.2	
42.7	68	1.2	27.0				
43.9	66	2.8	20.0	145	17	0.3	
48.0	46	4.0	47.5	169	17	0.3	
49.5	38	3.6	25.0	172	16	0.3	
54.4	23	1.2	34.0	308	28	0.8	
55.2	22	0.8	49.0	477	49	1.1	
67.2	15	0.2	0.2	632	17	7.7	

Dry basis.
Calculated as NO₂.

experiments also suggest a very low conversion of fuel-bound nitrogen into oxides of nitrogen. Dry soils averaged $1.9 \pm 2.0 \text{ g kg}^{-1}$, while wet soils averaged $1.5 \pm 1.6 \text{ g kg}^{-1}$ (all calculated as NO_2). The most interesting aspect here was the unusually high ratio of nitrogen dioxide (NO_2) to nitric oxide (NO). The concentration ratio of NO_2 to NO in most cases ranged between 5:1 and 10:1. One would expect the reverse to be true in most combustion experiments. Primary emission of NO_2 , although very unusual, is not unknown. Merryman and Levy⁽¹⁹⁾ have reported primary NO_2 in CO and hydrocarbon flames resulting from the reaction of nitric oxide with hydroperoxide (HO_2) radicals yielding NO_2 and OH. This reaction is possible in the slow combustion of highly oxygenated and moist fuels which would be expected to produce abundant quantities of the HO_2 radical.

Sulfur oxides (SO_x) were not determined in this study. However, earlier work by Benner,⁽³⁾ burning gram-size soil samples containing 0.25% sulfur, produced $0.6 \pm 0.5 \text{ g kg}^{-1}$ of sulfur dioxide. Benner also measured hydrogen sulfide (H_2S) emissions and found $1.8 \pm 1.3 \text{ g kg}^{-1}$ emitted. Benner used a hot wire technique to start and sustain combustion. He reported $44 \pm 9 \text{ g kg}^{-1}$ for TSP, $251 \pm 110 \text{ g kg}^{-1}$ for CO, $52 \pm 31 \text{ g kg}^{-1}$ for THC, and $3.9 \pm 2.1 \text{ g kg}^{-1}$ for NO_x .

Summary and Conclusions

Small blocks of organic soil (three wet, three dry) collected from south-central Florida were burned under controlled conditions in the laboratory. Once combustion was self-propagating, all samples burned to grey ash, even through layers with moisture contents of 135% of dry weight. Peak temperatures ranged from 416°C to 625°C .

Dry soils produced high TSP emission factors for the first 24 hours of burning ($30 \pm 20 \text{ g kg}^{-1}$) and low factors ($1 \pm \text{g kg}^{-1}$) for the later periods. The reverse was true for the wet soils; $4.1 \pm 3.8 \text{ g kg}^{-1}$ for the first 24 hours and $25 \pm \text{g kg}^{-1}$ for the later periods.

Carbon monoxide levels were high for all fires, averaging 269 g kg^{-1} . Total hydrocarbons averaged 23 g kg^{-1} and nitrogen oxides 1.7 g kg^{-1} . In a limited number of TSP samples analyzed for benzo(a)pyrene, the emission factor averaged $319 \mu\text{g kg}^{-1}$ and ranged from 13 to $1178 \mu\text{g kg}^{-1}$. The particulate matter produced from these fires was virtually all organic in nature (95% soluble in methylene chloride) and will be subjected to further chemical analysis.

Acknowledgements

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